

polyamides or polyesters of this invention may be viewed as three-dimensional, cross-linked materials comprising covalently bonded nanoscopic, hyperbranched domains which may be of the same or different chemical composition than the rest of the network. These materials may be formed into clear, highly transparent films, sheets, membranes, coatings or other objects, and may exhibit different glass transition temperatures that may rank them among either elastomers or plastomers. The materials may also exhibit high thermal stability, mechanical strength and toughness, and may offer new ways of preparing specialty membranes, protective coatings, photoresists, novel composites, controlled porosity materials, etc. Other applications may be found in biomedical areas, medical science and engineering, purification of liquids and gases, food processing, storage and packaging, printing and lithography, sensors, catalysts, etc. In many applications, such as coatings, the hyperbranched polymers may exhibit lower viscosity at any given solids content as compared with conventional compositions using linear or lightly branched polymers, and in contrast to dendrimers may exhibit desirable shear-thinning properties for certain applications.

The hyperbranched polyureas, polyurethanes, polyamidoamines, polyamides and polyesters of this invention may be subjected to surface modifications to provide a hydrophobic organosilicon exterior layer. The organosilicon layer can, for example, be formed by reacting an amine terminated polyurea, polyamidoamine or polyamide with a silicon-containing compound such as a carbosilane, silazine, silane, siloxane and combinations thereof. Examples include silanes or siloxanes of the respective formulae $\text{XSiR}_n\text{Y}_{(3-n)}$ or $\text{XR}_p\text{Y}_{(2-p)}\text{Si}(\text{OSiR}_2)_m\text{OSiR}_n\text{Y}_{(3-n)}$ wherein n represents zero or a positive integer; m represents zero, 1, 2 or 3; and p represents zero, 1 or 2. X is any group that reacts with a terminal amine, such as $\text{CH}_2=\text{CHCOO}(\text{CH}_2)_3-$, $\text{Cl}(\text{CH}_2)_3-$, $\text{Br}(\text{CH}_2)_3-$ or $\text{I}(\text{CH}_2)_3-$. Other groups that can react with an amine group, such as epoxy, $\text{ClCO}(\text{CH}_2)_3-$, $\text{ROCO}(\text{CH}_2)_3-$, or $\text{OCN}-\text{R}-$, wherein a in these groups represents an integer typically having a value of 1 to 6. Preferably each R is independently an alkyl radical containing 1 to 6 carbon atoms, most preferably methyl, an aryl radical such as phenyl, or a fluoroalkyl radical such as $-(\text{CH}_2)_2\text{CF}_3$ or $-(\text{CH}_2)_2(\text{CF}_2)_2\text{CF}_3$. Y represents a group that does not react with $-\text{NH}_2$ such as the vinyl group $\text{CH}_2=\text{CH}-$, the allyl group $\text{CH}_2=\text{CH}-\text{CH}_2-$, $-\text{OR}$, hydrogen, a triorganosiloxy radical, or a ferrocenyl radical.

Representative examples of organosilicon compounds that can be used herein include (3-acryloxypropyl) methyltrimethoxysilane, (3-acryloxypropyl) bis (vinyltrimethylsiloxy) methylsilane, (3-acryloxypropyl)tris (trimethylsiloxy)silane, iodomethyltrimethylsilane, chloromethyltrimethylsilane, or chloromethyltrimethylvinylsilane, etc. Similarly, hydroxyl terminated hyperbranched polyurethanes and hydroxyl terminated hyperbranched polyesters can be provided with an organosilicon outer layer by reaction with the above silanes or siloxanes, wherein X is any group that reacts with $-\text{OH}$, such as a carboxyl group or an isocyanate group. In an analogous manner, isocyanate terminated hyperbranched polyureas, isocyanate terminated hyperbranched polyurethanes, and carboxyl terminated hyperbranched polyesters can be reacted with silanes or siloxanes as set forth above, wherein X is a group that is reactive with the terminal groups of the hyperbranched polymers (e.g., isocyanate groups or carboxyl groups). The resulting organosilicon surface modified hyperbranched polyureas, polyurethanes, polyamidoamines, polyamides and polyes-

ters can be cross-linked by various mechanisms depending on the Y functional groups of the silanes or siloxanes. Possible cross-linking mechanisms include but are not limited to hydrosilation, hydrolysis/condensation reactions in the presence of moisture, or vinyl addition reactions.

The following examples are illustrative of particular embodiments of the invention.

EXAMPLE 1

Preparation of Amine-Terminated Hyperbranched Polyurea

A 500 mL round bottom flask was charged with tris(2-aminoethyl)amine (10.00 g, 0.0684 mol) and anhydrous THF (150 mL). The flask was flushed with N_2 for 2 minutes. The solution was cooled to -78°C , followed by dropwise addition of THF (anhydrous, 20 mL) solution of isophorone diisocyanate (IPDI) (7.60 g, 0.0342 mol) with stirring. It was stirred for 2 hours and then allowed to warm up to room temperature. It was further stirred at room temperature for 16 hours. THF solvent was removed by a rotavap to yield a sticky paste. The paste was washed with diethyl ether (2×20 mL), re-dissolved in 200 mL methanol and filtered. The filtrate was evaporated to dryness on rotavap and dried in vacuum for 16 hours. A white solid (12.37) designated as HB-IPDI- $(\text{NH}_2)_x$ was collected. ^1H NMR in CD_3OD : 0.94 ppm (s); 1.03 ppm(s); 1.05 ppm(s) overlapped with broad and weak multiplet ranging from 0.809 to 1.17 ppm; 1.58 ppm(b, m); 2.53 ppm(t); 2.74 ppm(t); 2.85 ppm(b, s); 3.11 ppm(b, s); 3.17 ppm(b, s); 3.32 ppm(s); 3.8 ppm(b); 6.21 ppm(b). Selected assignments of ^1H NMR spectrum: 0.94 ppm (s, CH_3); 1.03 ppm (s, CH_3); 1.05 ppm (s, C_8H_{17}); 2.53 ppm (t, $[-(\text{CH}_2)_2-]$); 2.74 ppm (t, $[-(\text{CH}_2)_2-]$); 3.21 ppm (s, $[-(\text{CH}_2)_3\text{C}_6\text{H}_6\text{CH}_2\text{NHCONH}-]$); 6.21 ppm (b and weak, $[(\text{NH})_2\text{CO}]$). $^{13}\text{C}\{^1\text{H}\}$ NMR in CD_3OD : 18.66 ppm (s); 24.07–24.55 ppm (m); 28.46 ppm (s); 29.26 ppm (s); 30.14 ppm (s); 30.71 ppm (b, m); 32.70 ppm (s); 32.93 ppm (s); 32.97 ppm (s); 35.96 ppm; 37.76 ppm (m); 39.24–39.99 ppm (m); 40.97 ppm(s); 41.79 ppm (s); 43.08 ppm(s); 43.60 ppm (s); 44.51 ppm(s); 45.60 ppm(s); 47.06 ppm(s); 47.92 ppm (s); 48.30 ppm (s); 50.63 ppm(s); 52.04 ppm(s); 55.03 ppm(s); 56.10 ppm(s); 56.66 ppm(s); 56.98 ppm(s); 57.07 ppm(s); 57.16 ppm(s); 58.19 ppm(s); 58.38 ppm (s); 160.69 ppm(s); 161.57 ppm(s); 165.90 ppm (s); 166.00 ppm(s). Selected assignments in $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum: 18.66 ppm (s, $[\text{O}(\text{CH}_2\text{CH}_3)_2]$); 24.07–24.55 ppm (m, CH_3); 28.46 ppm (s, CH_3); 29.26 ppm (s, CH_3); 30.14 ppm (s, CH_3); 30.71 ppm (b and m, CH_3); 35.96 ppm (s, CH_3); 39.24–39.99 ppm (m CH_2); 40.97 ppm (s, CH_2); 41.79 ppm (s, CH_2); 43.08 ppm (s, CH_2); 43.60 ppm (s, CH_2); 45.60 ppm (s, CH_2); 47.06 ppm (s, CH_2); 47.92 ppm (s, CH_2); 48.30 ppm (s, CH_2); 50.63 ppm (s, CH_2); 52.04 ppm (s, CH_2); 55.03 ppm (s, CH_2); 56.10 ppm (s, CH_2); 56.66 ppm (s, CH_2); 56.98 ppm (s, CH_2); 57.07 ppm (s, CH_2); 57.16 ppm (s, CH_2); 58.19 ppm (s, CH_2); 58.38 ppm (s, CH_2); 44.51 ppm [s, (CH) in cyclohexyl]; 160.69 ppm [s, $(-\text{NHCONH}-)$]; 161.58 ppm [s, (NHCONH)]; 165.89 ppm [s, (NRCONH)]; 166.00 ppm [s, (NHCONH)]. IR on KBr pellet (selected peaks): 3353 cm^{-1} [broad and strong, $\nu(-\text{NH}_2)$ and $\nu(-\text{NH}-)$]; 1643 cm^{-1} [strong, $\nu(\text{C}=\text{O})$]; 1566 cm^{-1} [strong, $\nu(\text{CNH})$ of amide]. MALDI-TOF (matrix: 2,5-Dihydroxybenzoic acid): 12 apparent groups (550.8 m/z, 740.0 m/z, 904.2/z, 1095.5 m/z, 1249.6 m/z, 1429 m/z, 1604.5 m/z, 1785.4 m/z, 1958.4 m/z, 2145.6 m/z, 2321.8 m/z, 2508.0 m/z) within the total range from 500 to 3200 m/z together with some weak groups at two ends of the range. GPC[Column set: Plgel C(2X) (at 80°C). Solvent: NMP(0.1% LiBr), Detector DRI (50°C). Standards: polystyrene 800–300,000]: Mn 564. Mw 831. Polydispersity 1.44.